

"Ionic Radii," Spin-Orbit Coupling and the Geometrical Stability of Inorganic Complexes*

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The van Santen and van Wieringen theory of "ionic radii" is briefly reviewed and extended to include spin-orbit influences. It is noted that, although for the most part spin-orbit forces have little effect upon stereochemical predictions made for the first transition series, noteworthy exceptions to this rule occur for octahedral complexes of Co^{++} and tetrahedral complexes of Ni^{++} and Cu^{++} . Indeed, it is found that spin-orbit coeffects render the ground states of these molecules Jahn-Teller resistant. Diagrams are displayed and tables compiled to illustrate the variation of ionic radii with atomic number for the second and third transition series. Paths for future theoretical research are indicated and an exhortation for closer theoretical-experimental alliance is promulgated.

Now, although the ligand field theory is in its 30th year, it has only been within the last decade that its chemical fruits have been earnestly harvested. One of the earliest pickings of its ripened orchards was accomplished by van Santen and van Wieringen.¹ These researchers noticed that the enigmatic irregularities of the existent transition metal "ionic-radii" tabulations could be neatly rationalized on the basis of the Bethe-Kramers-Van Vleck^{2,3,4} crystalline field formalism. I now wish to extend their argument to include metals which possess a nonnegligible spin-orbit interaction and to point out certain modifications (due to Jahn⁵) of the Jahn-Teller stability rules⁶ which such interactions engender. But before we may embark upon this tour of the crystallographic implications of the existence of spin-orbit forces in inorganic complexes, it is necessary to review briefly the basic precepts of ligand (or crystalline) field theory.

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If a positive rare gas core is placed in the midst of an octahedral arrangement of negative (or neutral) ligands (see Fig. 1), a mutual electrical polarization of these two sets of charge clouds occurs. With the concomitant shifting of ligand electrical charge toward the central metal ion, driven by the "charge neutrality" forces, the ligand molecular orbitals attain a partially metallic character. Conversely, the central metal ion orbitals, *both occupied and unoccupied*, partake of the surrounding ligand charge density distribution (Fig. 1).^{*} *This reciprocity of electronic charge induces a separation of the as yet unoccupied nd-like, ($n = 3, 4, 5$), orbitals of the central (rare gas-like) ion.* In covalent bonding terminology these latter orbitals become antibonding in nature, dividing themselves into two groups: the σ -antibonding e_g molecular orbitals, which originate from the $nd_{x^2-y^2}$ and nd_{z^2} atomic electron distributions, and the π -antibonding t_{2g} molecular orbitals, which proceed from the atomic nd_{xy} , nd_{yz} , and nd_{xz} charge dispositions (see Fig. 2).

When the atomic number of the metallic core is increased so that additional electrons become available to the complex, the empty antibonding t_{2g} and e_g orbitals are sequentially filled. Now, from general electro-

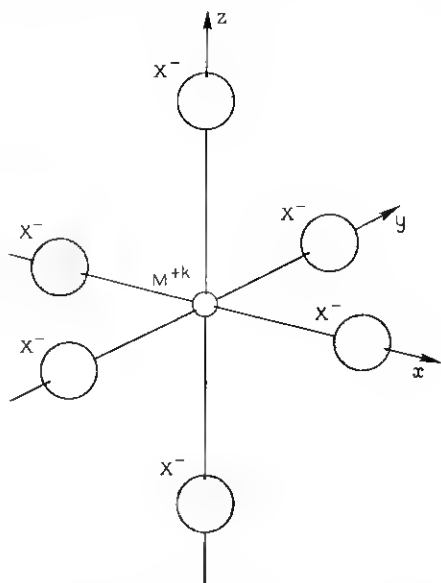


Fig. 1 — Geometrical disposition of an octahedral complex.

^{*} We should here like to suggest the use of the words *addend* (that which adds) and *augend* (that which augments) as appropriate synonyms for ligand (that which ligates).

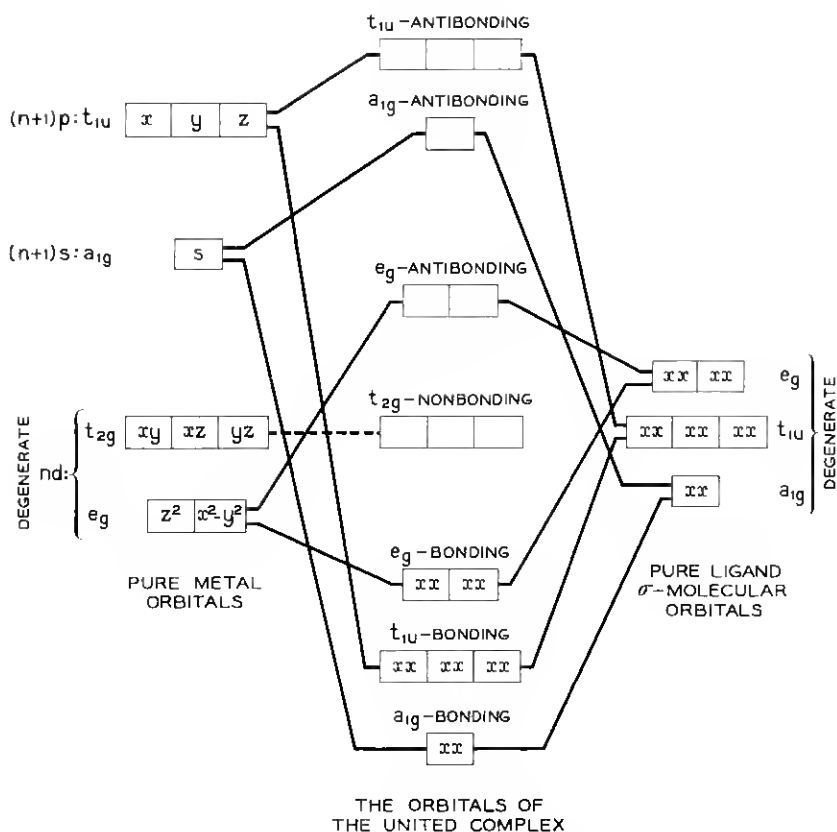


Fig. 2 — Energy levels of a σ -bonded octahedral complex. When π -bonding is added, the empty t_{2g} orbital becomes π -antibonding in character.

static considerations we would expect an attendant smooth (monotonic) decrease of "ionic radii" with the increasing charge of the core, as is shown in Fig. 3. But this is not the case in actuality! "Real" ionic radii vary in the jagged fashion pictured in Fig. 4. What van Santen and van Wieringen were able to show is that the observed irregularity of the "ionic radii" behavior was due to the serial occupancy of the antibonding t_{2g} and e_g orbitals: that the occupancy of the weakly antibonding xy , xz , and yz -type orbitals allowed a *contraction* of the bonding radii and that the population of the strongly antibonding x^2-y^2 - and z^2 -type orbitals forced an *expansion* of the bonding radii for octahedral complexes. This situation is emphasized by the registration of their results given in Table I. In addition, the theorem of Jahn and Teller, in the

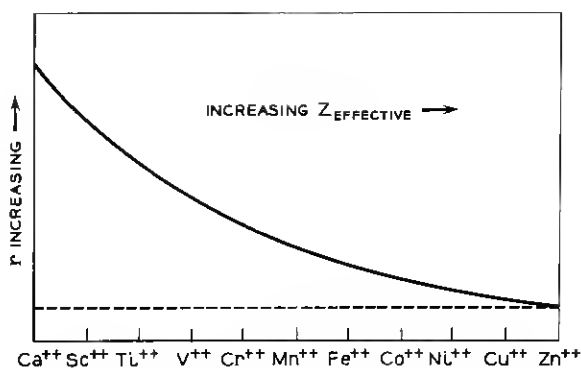


Fig. 3 — Expected variation of "ionic radius", r , with effective nuclear charge, $Z_{\text{effective}}$.

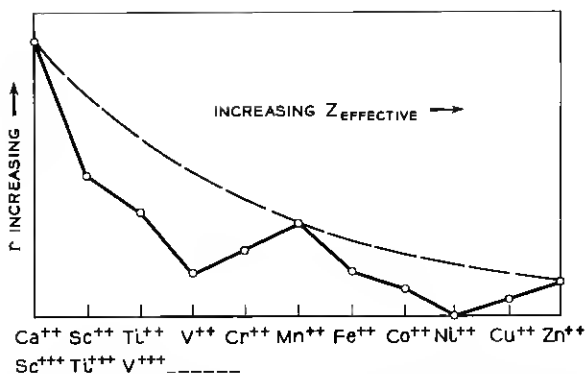


Fig. 4 — Variation of "ionic radius" with effective nuclear charge for octahedral geometries. The maxima and minima of the curves are states of perfect cubic ("pseudo spherical") symmetry.

TABLE I

Free Ion Ground State.....	$1S$ d^0	$2D$ d^1	$3F$ d^2	$4F$ d^3	$5D$ d^4	$6S$ d^5	$5D$ d^6	$4F$ d^7	$3F$ d^8	$2D$ d^9	$1S$ d^{10}
Configuration.....											
Crystal Ground State in an Octahedral Field.....	$1A_{1g}$	$2T_{2g}$	$3T_{1g}$	$4A_{2g}$	$5E_g$	$6A_{1g}$	$5T_{2g}$	$4T_{1g}$	$3A_{2g}$	$2E_g$	$1A_{1g}$
Number of e_g Electrons.....	0	0	$\frac{1}{5}$	0	1	2	2	$2\frac{1}{5}$	2	3	4
Number of t_{2g} Electrons.....	0	1	$1\frac{1}{5}$	3	3	3	4	$4\frac{1}{5}$	6	6	6

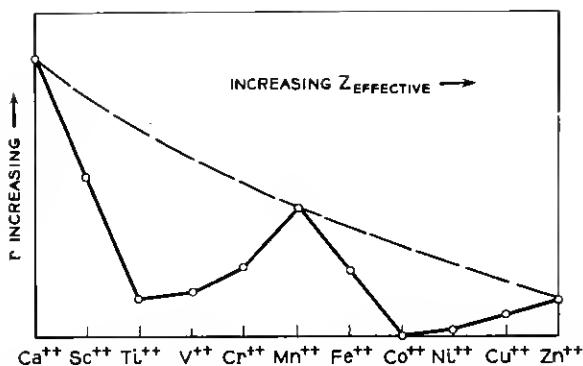


Fig. 5 — Variation of "ionic radius" with effective nuclear charge for tetrahedral environs. The maxima and minima of the curves are states of perfect cubic ("pseudo spherical") eurythmy.

TABLE II

Free Ion Ground State	$1S$	$2D$	$3F$	$4F$	$5D$	$6S$	$6D$	$4F$	$3F$	$2D$	$1S$
Configuration	d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Crystal Ground State in a Tetrahedral Field ..	$1A_1$	$2E$	$3A_2$	$4T_1$	$5T_2$	$6A_1$	$5E$	$4A_2$	$3T_1$	$3T_2$	$1A_1$
Number of t_2 Electrons	0	0	0	$1\frac{1}{2}$	2	3	3	3	$4\frac{1}{2}$	5	6
Number of e Electrons	0	1	2	$1\frac{1}{2}$	2	2	3	4	$3\frac{1}{2}$	4	4

hands of Van Vleck⁷ and others, predicted that octahedral complexes with an odd number of electrons in the antibonding e_g shell [e.g. Cr^{++} and $\text{Mn}^{+++}(d^4)$ and $\text{Cu}^{++}(d^9)$] should be permanently distorted. Conclusions of a similar nature were also obtained for tetrahedral complexes (Fig. 5 and Table II).

How does the complication of spin-orbit coupling modify these results? Simply in this way: The linkage of the spin and orbital magnetic moments serves to split the six-fold degenerate t_{2g} states [three possible orbital motions and two possible spin directions] into a four-fold level called $\gamma_8(t_{2g})$ (by Bethe²) and a two-fold level called $\gamma_7(t_{2g})$. The four-fold multiple of spin-orbit states, e_g , remains intact, and also takes on the new label $\gamma_8(e_g)$. The sequence of antibonding orbitals in octahedral and tetrahedral complexes then becomes as shown in Fig. 6.*

* At this juncture, we should like to propose that the Mulliken notation, (a , e , t , etc.), be reserved for pure orbital states, and the Bethe notation, γ_j , ($j = 1, 2, \dots, 8$), for spin-orbital configurations.

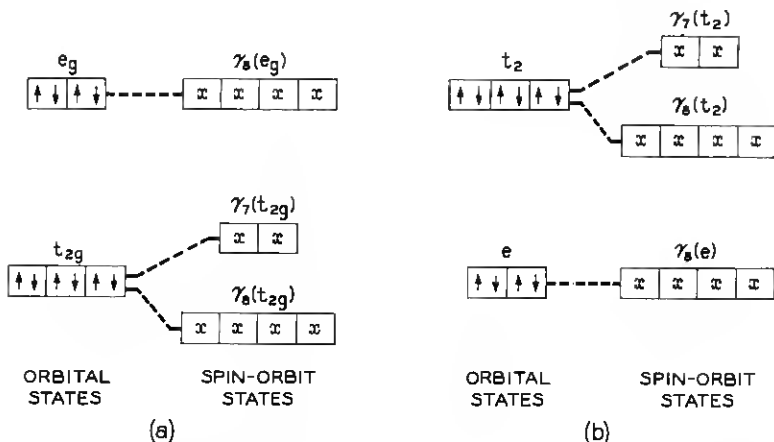


Fig. 6 — Correlation of the orbital and spin-orbit states of (a) octahedral and (b) tetrahedral inorganic complexes.

For the most part, the entrance of spin-orbit correlations has no effect upon stereochemical predictions made for the first transition series. Notable exceptions to this rule occur for octahedral complexes of Co^{++} and tetrahedral complexes of Ni^{++} and Cu^{++} . Both octahedral Co^{++} , which subsumes the configuration $\gamma_8(t_{2g})^4\gamma_7(t_{2g})^1\gamma_8(e_g)^2$ in our naïve theory, and tetrahedral Cu^{++} , which takes on the assignment

$$\gamma_8(e_g)^4\gamma_8(t_{2g})^4\gamma_7(t_{2g})^1,$$

exist in the Jahn-Teller *resistant* electronic dispositions, Γ_6 and Γ_7 respectively [according to Jahn,⁵ the doubly degenerate (cubic) spin-orbit states of Bethe, Γ_6 and Γ_7 , the so-called Kramers doublets, can *not* exhibit (pure) Jahn-Teller conformational instability]. Since the nearest-lying electronic states are ~ 400 (Shulman⁸) and ~ 1000 cm^{-1} (Liehr⁹) away for Co^{++} and Cu^{++} , respectively, their ground electronic states are also *not* susceptible to large pseudo Jahn-Teller coercions, and should thus be stable in the regular polyhedral arrangement. Similarly, tetrahedral Ni^{++} , which has the electron distribution $\gamma_8(e_g)^4\gamma_8(t_{2g})^4$ in the simple one-electron scheme, exists in the totally symmetric (nondegenerate) state, Γ_1 , in which the Jahn-Teller forces are again inoperative. Since the closest electronic disposition, which under nuclear displacements might perturb the ground state conformational regularity, is ~ 300 cm^{-1} distant (Liehr and Ballhausen¹⁰), Ni^{++} should also *not* exhibit any large pseudo Jahn-Teller distortions, and thus should be stable in the regular tetrahedral form. Moreover, since the Bethe states Γ_1 , Γ_6 and Γ_7

are "pseudo spherical" (and the only Jahn-Teller impotent states possible for cubic environs), they should fit into such selective crystallographic structures as the garnets, into which only the most highly symmetric ions may enter. Garnet structures of this type have been prepared by Seymour Geller and Alten Gilleo at Bell Telephone Laboratories; however, a complete analysis of the ionic site symmetries is still in progress, and so no definite conclusions are yet available.* It is interesting to note, though, that CoO and Co^{++} dissolved in MgO are perfectly octahedral (Low¹¹), and that single crystals of KCoF_3 (recently characterized by Kerro Knox of Bell Telephone Laboratories) also contain regular octahedral Co^{++} clusters.†

A much different story unfolds for complexes of the second and third transition series. Here the separation of the $\gamma_7(t_{2g})$ and $\gamma_8(t_{2g})$ levels which arise from the π -antibonding (orbital) t_{2g} state of octahedral complexes may become large enough so that electronic repulsions do not disturb the orderly filing of the levels. Hence, the orbitals tend to fill up with the first four electrons going into the lowest $\gamma_8(t_{2g})$ level, the next two into the $\gamma_7(t_{2g})$ orbit, and the next four into the highest $\gamma_3(e_g)$ level, for octahedral complexes; and the two $\gamma_3(e)$ and $\gamma_8(t_2)$ trajectories are occupied first for tetrahedral complexes and the $\gamma_7(t_2)$ level last. In Figs. 7 and 8 and Tables III and IV we summarize the structural chem-

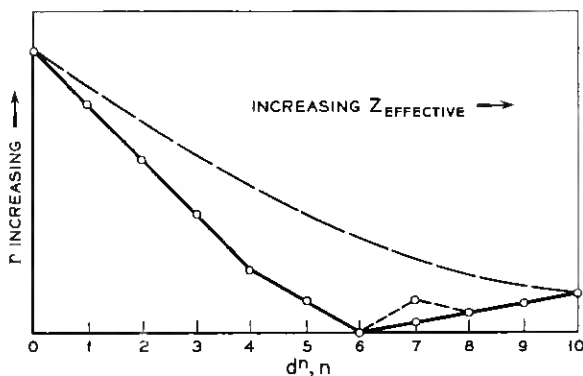


Fig. 7 — Variation of "ionic radius" with effective nuclear charge for medium-strong spin-orbit coupled octahedral complexes. The configurations d^n , ($n = 0, 4, 5, 6, 7, 10$) are states of perfect cubic ("pseudo spherical") symmetry. The states d^3 and d^8 are but slightly asymmetric due to their spin distributions.

* Co^{++} is now known to enter into octahedral garnet sites (Geller¹²).

† The large reduction in magnitude of the Jahn-Teller forces in FeO and Fe^{++} dissolved in MgO (Low¹¹), and in KFeF_3 (Knox¹³) is also explicable on the basis of a (partial) spin-orbit stabilization (Van Vleck¹⁴).

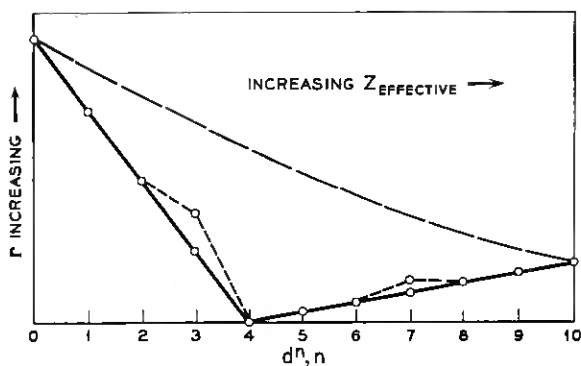


Fig. 8 — Variation of "ionic radius" with effective nuclear charge for medium-strong spin-orbit coupled tetrahedral complexes. The configurations d^n , ($n = 0, 4, 8, 9, 10$) are states of perfect cubic ("pseudo spherical") eurythmy. The states d^2 and d^7 are but slightly asymmetric due to their spin distributions [the same may be said for d^6 if it exhibits *maximum* spin].

ical expectations for ions of the second and third (especially the third) transition series. The ups and downs of the radii plots in these figures follow immediately upon the determination of the population of the t_{2g} -like and e_g -like spin-orbitals $\gamma_8(t_{2g})$, $\gamma_7(t_{2g})$, and $\gamma_8(e_g)$; just as was the case for the original van Santen and van Wieringen theory.

The exact nature of the distribution of electrons amongst the various tetrahedral levels depends upon whether the ligand field is very strong or not. We have therefore listed both the maximum and minimum spin cases for some of the "ions" (all electron populations are taken to be integral). One interesting result of the above tabulations is that the introduction of spin-orbit interactions geometrically stabilizes the regular polyhedral structure for a larger number of compounds than does the absence of such influences. In passing, it should be mentioned that

TABLE III

Free Ion Ground State.....	$1S$	$2D$	$3F$	$4F$	$5D$	$6S$	$5D$	$4F$	$3F$	$2D$	$1S$
Configuration....	d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Crystal Ground State in an Octahedral Field..	Γ_1	Γ_3	Γ_3	Γ_8	Γ_1	Γ_7	Γ_1	Γ_6 or Γ_8	Γ_5	Γ_8	Γ_1
Number of $\gamma_8(e_g)$ Electrons.....	0	0	0	0	0	0	0	2 or 1	2	3	4
Number of $\gamma_7(t_{2g})$ Electrons.....	0	0	0	0	0	1	2	1 or 2	2	2	2
Number of $\gamma_8(t_{2g})$ Electrons.....	0	1	2	3	4	4	4	4	4	4	4

TABLE IV

Free Ion Ground State..... Configuration... Crystal Ground State in a Tetrahedral Field..	1S d^0	2D d^1	3F d^2	4F d^3	5D d^4	6S d^5	5D d^5	4F d^6	3F d^7	2D d^8	1S d^{10}
	Γ_1	Γ_8	Γ_8	Γ_8	Γ_1	Γ_8	Γ_3 or Γ_8 (?)	Γ_8	Γ_1	Γ_7	Γ_1
Number of $\gamma_7(t_2)$ Electrons.....	0	0	0	0	0	0	0	1 or 0	0	1	2
Number of $\gamma_8(t_2)$ Electrons.....	0	0	0	1 or 0	0	1	2	2 or 3	4	4	4
Number of $\gamma_8(e)$ Electrons.....	0	1	2	2 or 3	4	4	4	4	4	4	4

a possible test of the foretold octahedral "ionic radii" demeanor would be afforded by the structural determination of the gaseous WF_6 , ReF_6 , etc., series of compounds.

To firmly pin down the stereochemical deportment of transition metal complexes, a good deal more work must be done, especially upon the d^n , ($n = 3, 4, 6, 7$), configurations for strong spin-orbit forces. Carl Ballhausen and myself are presently investigating the $d^{3,7}$ case; we hope that others will extend our results to encompass the $d^{4,6}$ situation also. At this point we are in a position to witness a veritable mushrooming of theoretical and theoretically inspired experimental research in the field of transition metal, rare earth and actinide complex chemistry. I sincerely hope that this close collaboration of the theoretical and experimental inorganic chemist will indeed come to pass.*

ACKNOWLEDGMENTS

I should very much like to thank Seymour Geller, Kerro Knox and Robert G. Shulman for illuminating discussions of their researches on similar topics, and F. Albert Cotton, Dieter Gruen, William Low, Ronald S. Nyholm and Herbert A. Weakliem, Jr., for prepublication information concerning their researches in this area.

* *Note added in proof:* A revised set of ionic radii for M^{+3} ions has been formulated by Geller,¹⁸ and for M^{+2} ions by Knox,¹³ which agree quite nicely with the theory outlined in this paper. Mr. Geller informs me that the Ti^{+3} radius reported in his article should, on the basis of recent measurements¹⁶ on $LaTiO_3$, now read 0.633 angstrom. Also, it is interesting to note that Gill and Nyholm¹⁷ have recently prepared some truly tetrahedral complexes of divalent nickel, which serve to substantiate the results obtained in melts of $NiCl_2$.^{18,19} The present status of tetrahedral Ni^{+2} chemistry is completely outlined in the recent paper of Cotton, Faut and Goodgame.²⁰ Racah, Schonfeld and Low²¹ and Weakliem²² have recently completed the "exact" calculation of the energy levels of $d^{3,7}$ complexes; therefore, the original computation planned for these systems by Carl Ballhausen and myself has understandably been abandoned.

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